

UHTC Composites for Leading Edges

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Ultrahigh temperature ceramics (UHTC) have performed unreliably due to material flaws and attachment design. These deficiencies are brought to the fore by the low fracture toughness and thermal shock resistance of UHTC. In addition, poor oxidation resistance is a limitation on UHTC applicability to reusable launch vehicles. We have been addressing these deficiencies for the past two years via a small task at GRC that is in the Airframe part of the Next Generation Launch Technology Program. Our focus is on UHTC composite (UHTCC) constructions and functional grading to address the mechanical issues and on composition modification to address the oxidation issue. Processing, mechanical property, and oxidation results will be reported.

Outline

- Introduction
- Objectives
- UHTCC Description
- Results
 - Flexural tests
 - Furnace oxidation
 - Torch tests
- Conclusions
- Recommendations

Keywords: refractory materials, ceramic composites, flexural strength, thermal shock, oxidation resistance

Prepared for:

2004 National Space & Missile Materials Symposium (NSMMS),
Seattle, Washington, June 21 - 25, 2004

NGLT
NEXT GENERATION LAUNCH TECHNOLOGY

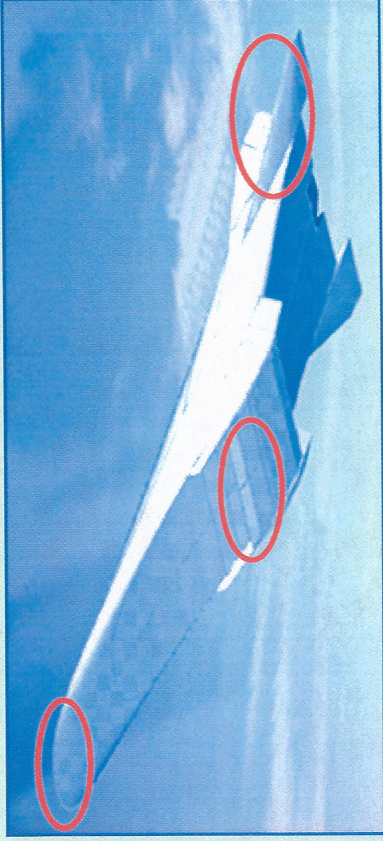
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Introduction



Key Issues

- ◆ Thermal stress resistance
- ◆ Oxidation resistance
- ◆ Temperature capability
- ◆ Architecture optimization



Goal

- ◆ Develop UHTCC for $\geq 3600^{\circ}\text{F}$, reusable, hypersonic vehicle leading edges

Oxidation Resistant Coating

Functionally Graded
Transition

UHTC Composite
Core

Objectives

- ◆ Characterize a UHTC composite plate fabricated by Starfire Systems, Inc.
 - CAVEAT: Recognize that little or no development effort went into fabrication of this material. It was a best effort fabrication for NASA LaRC
- ◆ Reveal some of the issues associated with the UHTCC concept

Composite Constituents and Processing

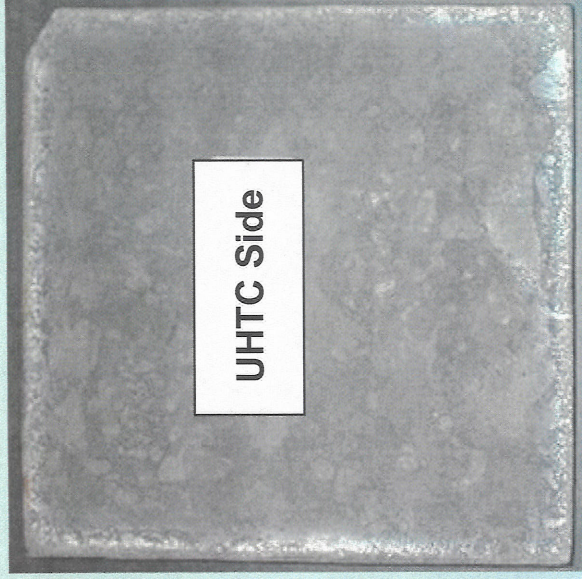
Constituents

- ◆ Zoltek Panex® 30 Carbon Fabric PW06
- ◆ Starfire Systems' SP-Matrix Polymer (Allylhydridopolycarbosilane (AHPCS))
- ◆ HfB₂ Powder
- ◆ SiC Powder

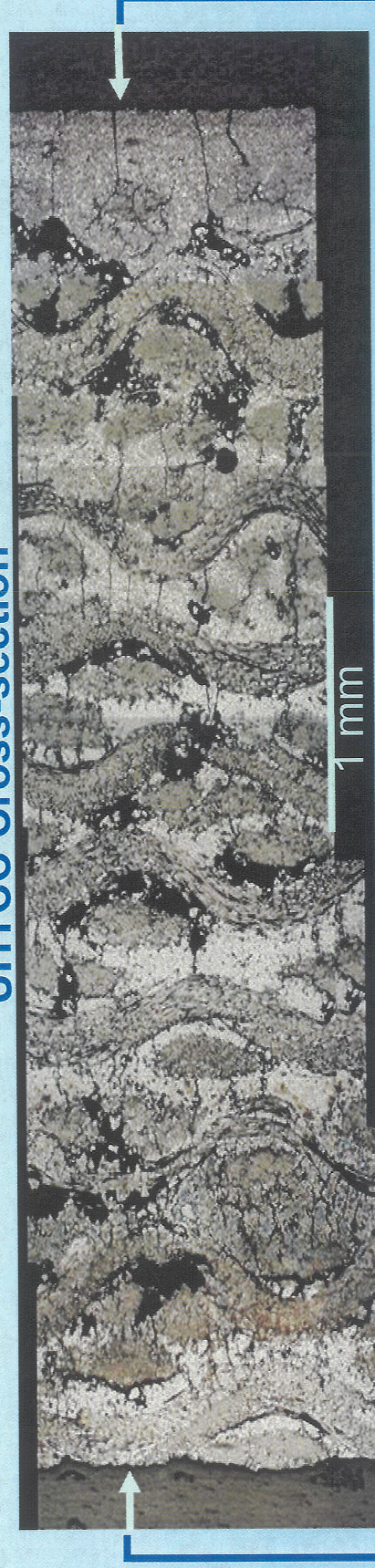
Processing of Part Number 000928-6-64

- ◆ **Initial Cycle:**
 - For the initial lay up the **bottom 6 layers of cloth** are coated
 - **with a SiC/AHPCS slurry** and the **top 5 layers** are coated
 - **with a HfB₂ /AHPCS slurry** and assembled in a mold.
 - Cured to 400°C and fired to 850°C under inert gas to pyrolyze.
- ◆ **Cycle 2:**
 - **Coat the HfB₂ side of the plate with more HfB₂ /AHPCS slurry.**
 - Fire directly to 850°C under inert gas.
- ◆ **Cycle 3: Repeat cycle 2**
- ◆ **Cycle 4 - 10:**
 - **Vacuum infiltrate with AHPCS only.**
 - Pyrolyze directly to 850°C under inert gas, no clamping necessary.

UHTCC Plate Appearance and Specimen Map

[illegible]

UHTCC Cross-section

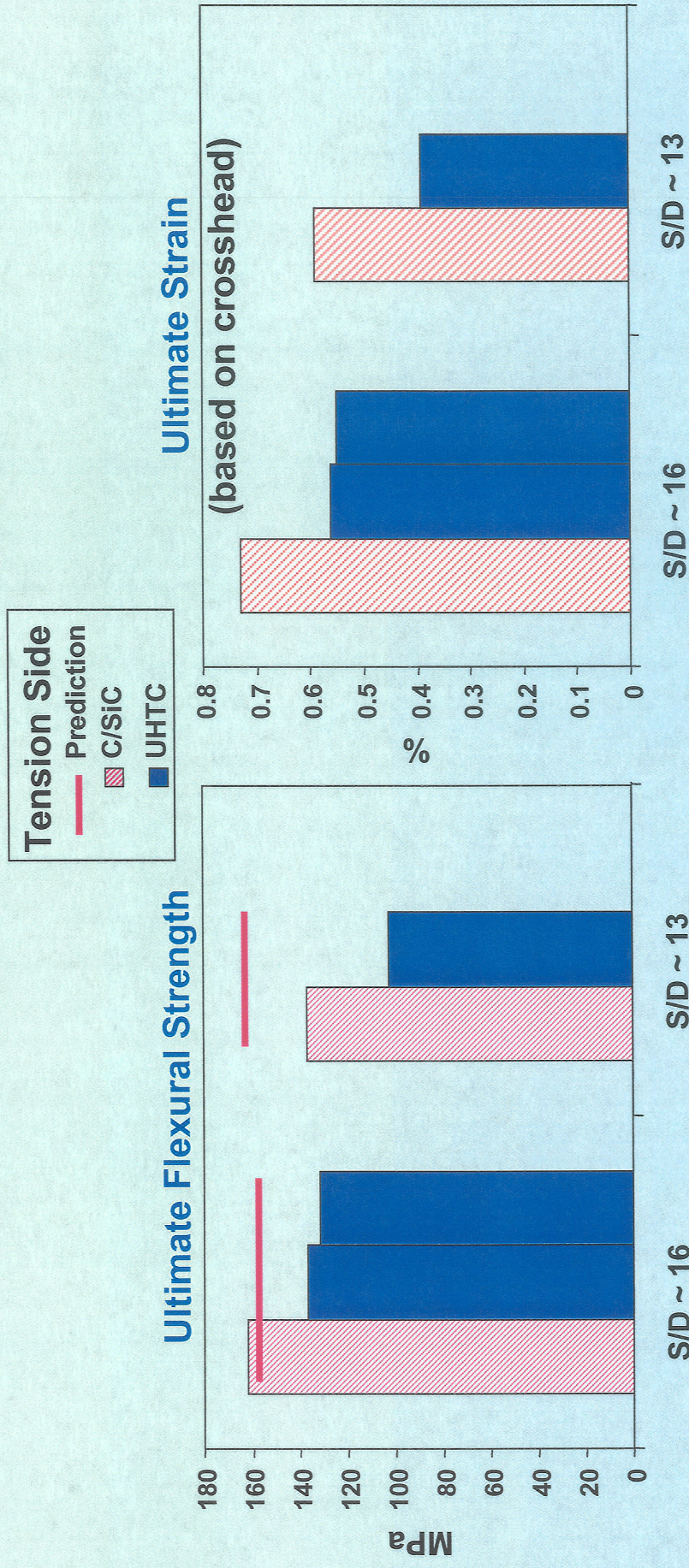


sic. C

Phases Detected by XRD

 HfB_2

UHTCC Flexural Strength Results

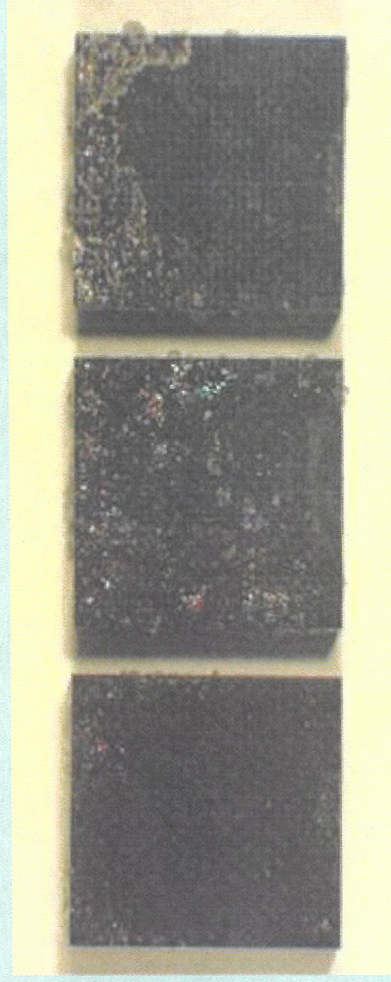


Predictions Based on Beam Theory

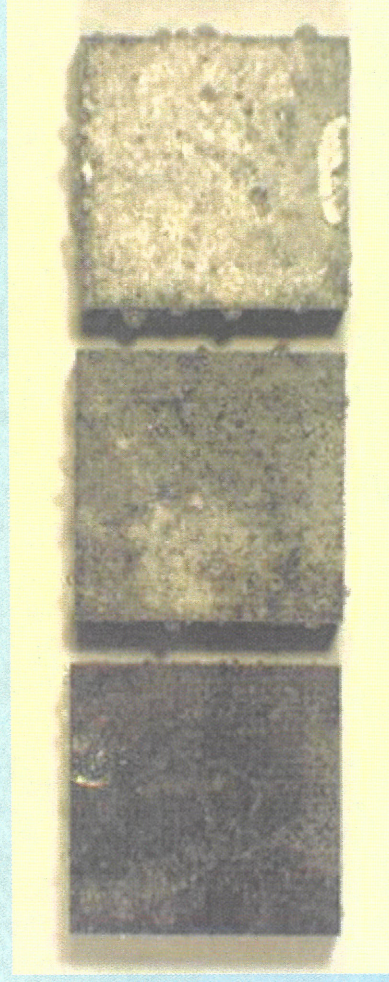
- ♦ Calculated load at 0.7% strain
- ♦ Panex 30 minimum property: $E = 193 \text{ GPa}$
- ♦ Rule of mixtures with no matrix contribution

UHTCC After 1627°C Furnace Oxidation

C/SiC
Side

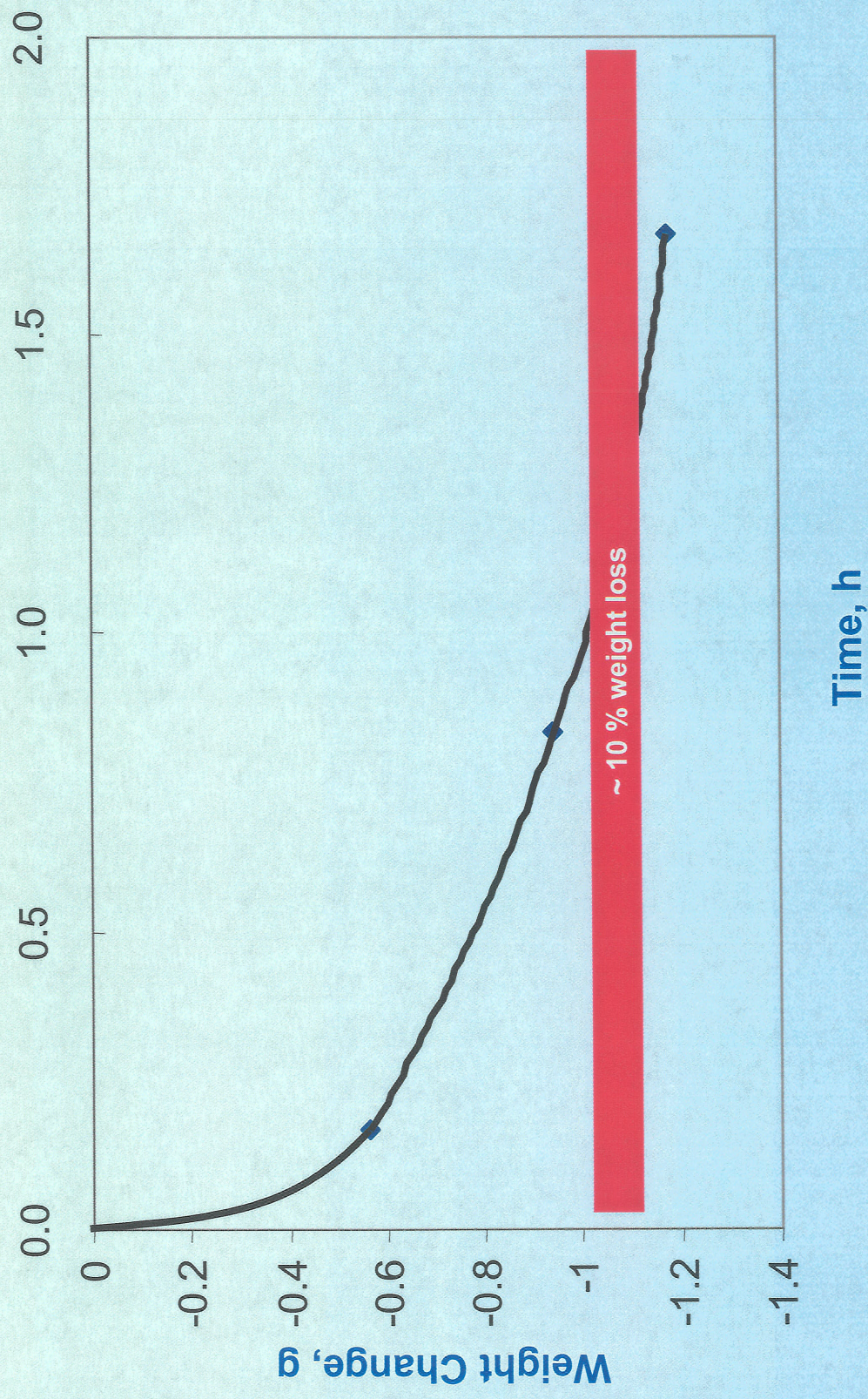


HfB₂
Side



Cycles	1	5	10
Hours	0.167	0.833	1.667

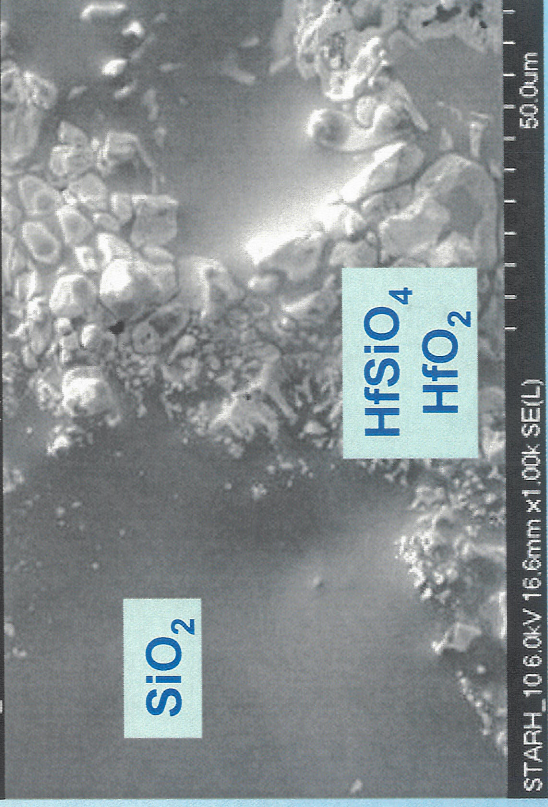
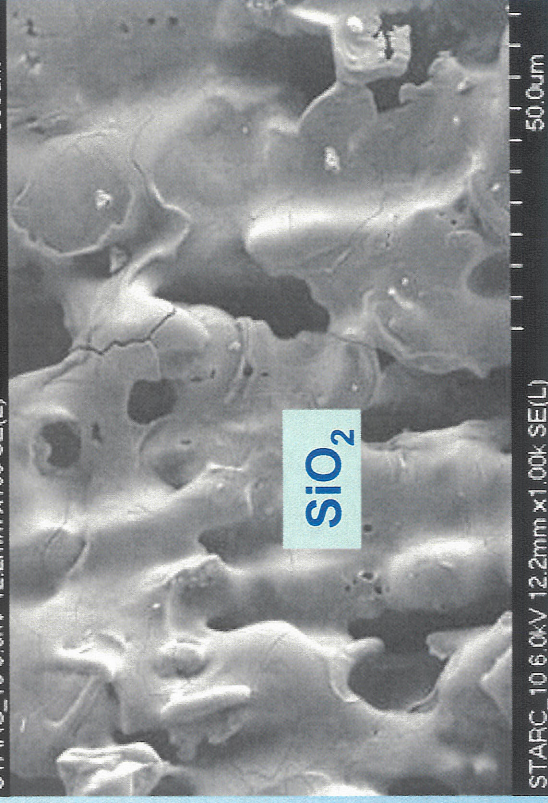
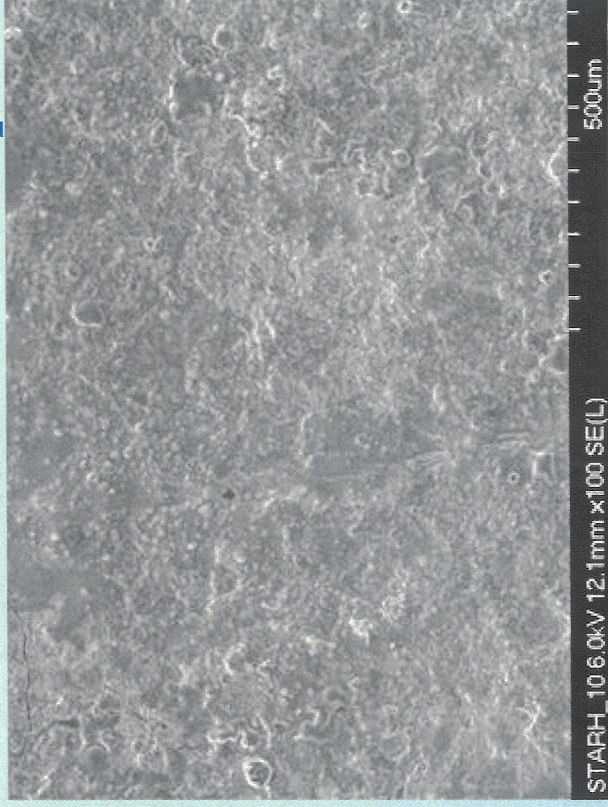
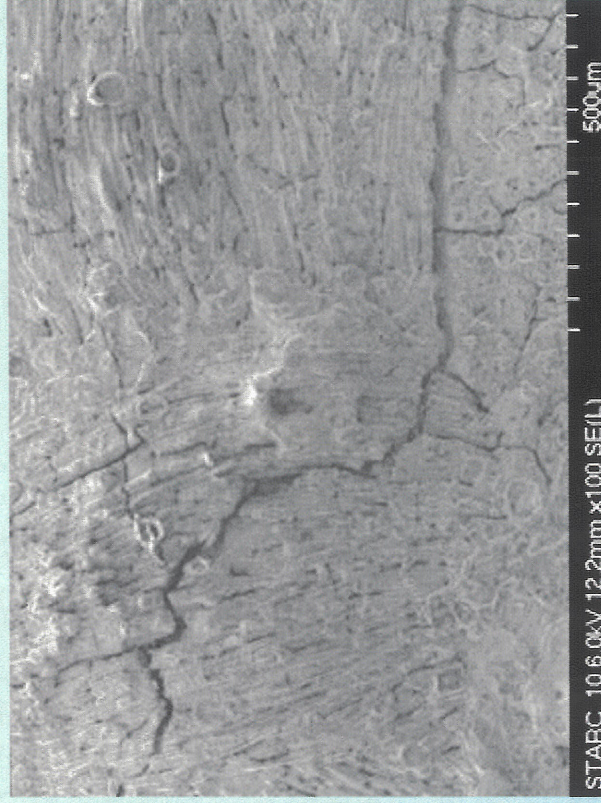
Furnace Oxidation of UHTCC at 1627°C



UHTCC After 10 Ten-minute Furnace Oxidation Cycles in Air at 1627°C

C/SiC Side

HfB₂ Side



SiO₂

SiO₂

HfSiO₄
HfO₂

UHTCC Oxy-Acetylene Torch Test

- ◆ Sample O: One 4 min. cycle to 1805°C
 - Weight loss = 0.79 g, or 1.9%
- ◆ Sample N: Three ~4 min. cycles
 - Cycle 1 max temp 1815°C
 - Cycle 2 max temp 1915°C
 - Cycle 3 max temp 2015°C
 - Weight loss = 1.95 g, or 4.6%

Sample O	
Time, min.	Temp, °C
0.5	1720
1.0	1750
1.5	1750
2.0	1755
2.5	1765
3.0	1775
3.5	1790
4.0	1805



0 sec

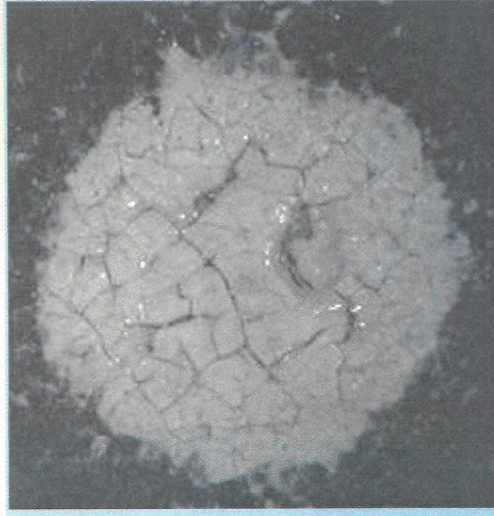
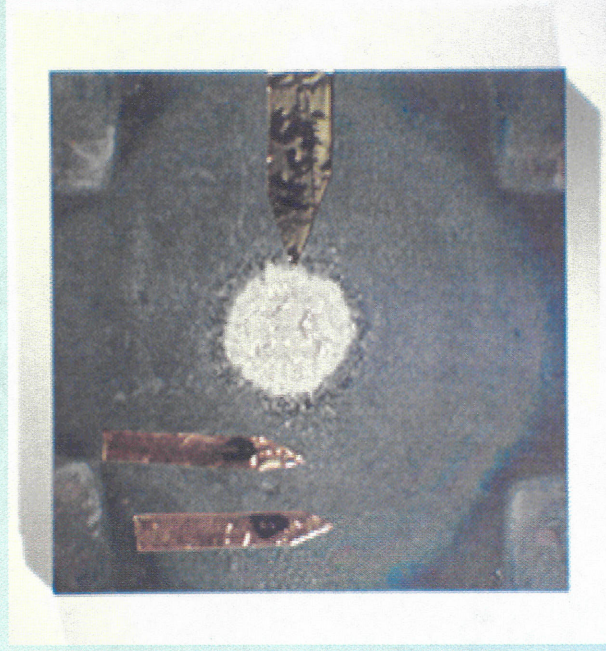
10 sec

20 sec

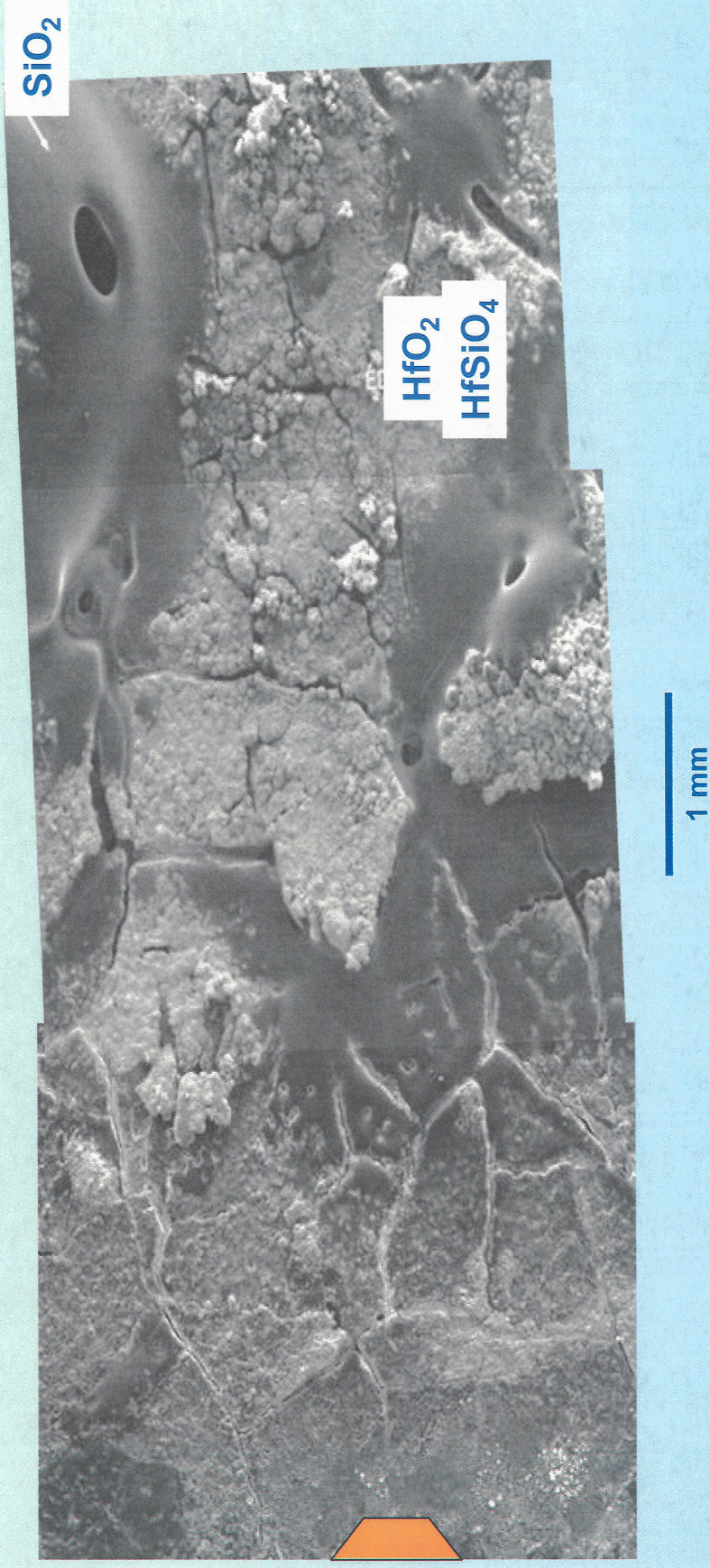
30 sec

Specimen "O" during cool-down

UHTC Surface After Three 4-Minute Torch Cycles to 1815 to 2015°C



SEM of Center of UHTC Surface After Three Torch Cycles

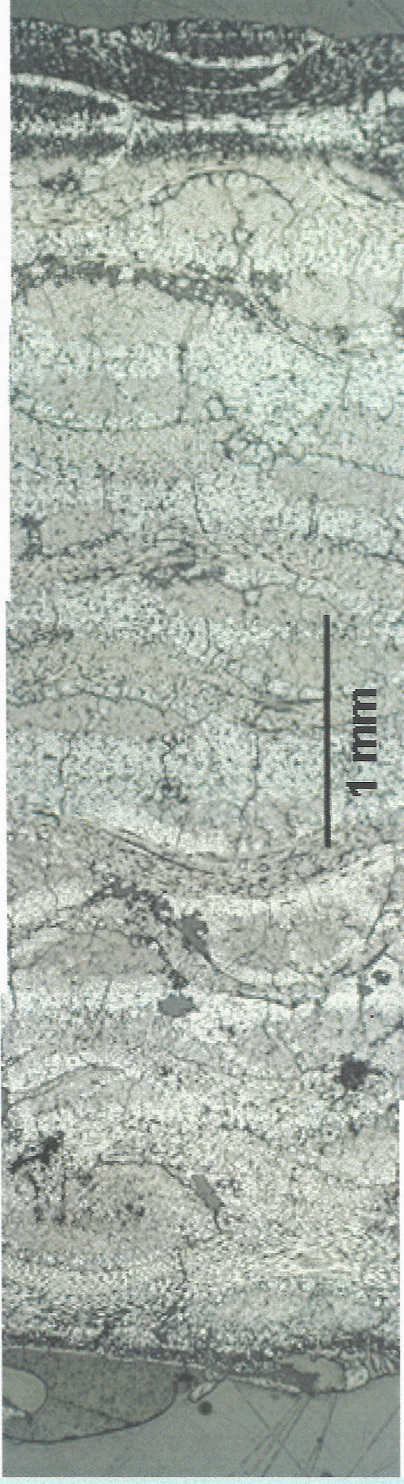


Microcracked oxide scale contains many large pores

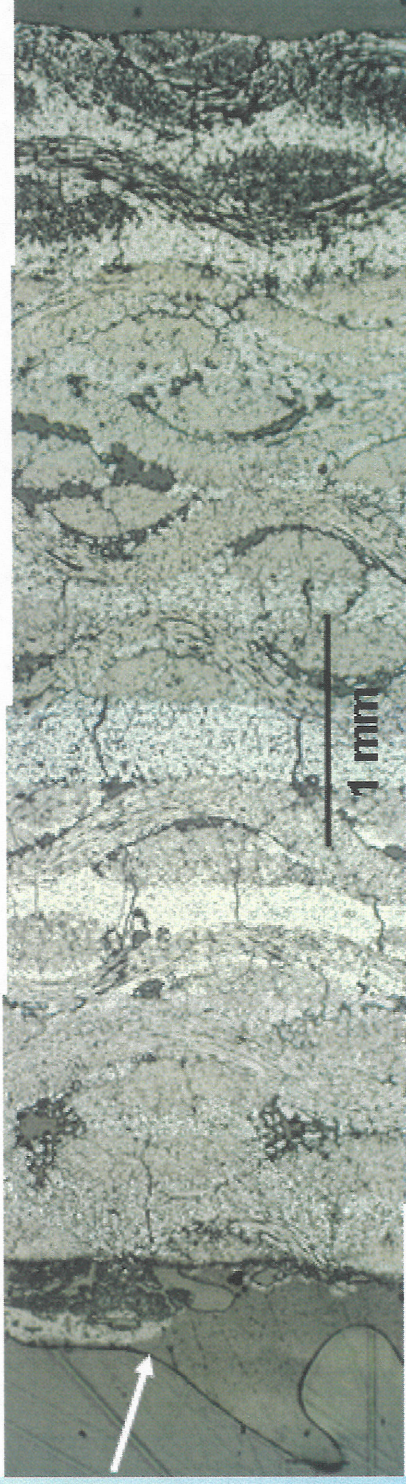
UHTCC Cross-sections After Torch Exposures

C/SiC Side

UHTC Side



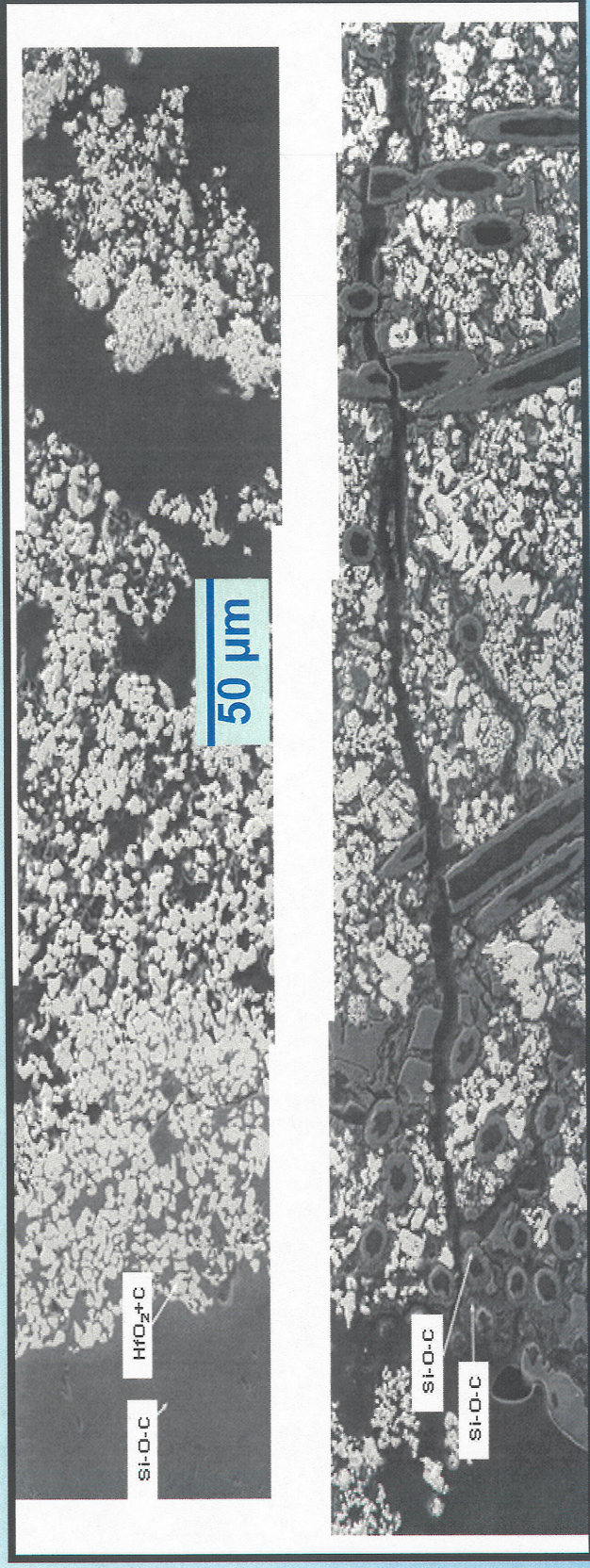
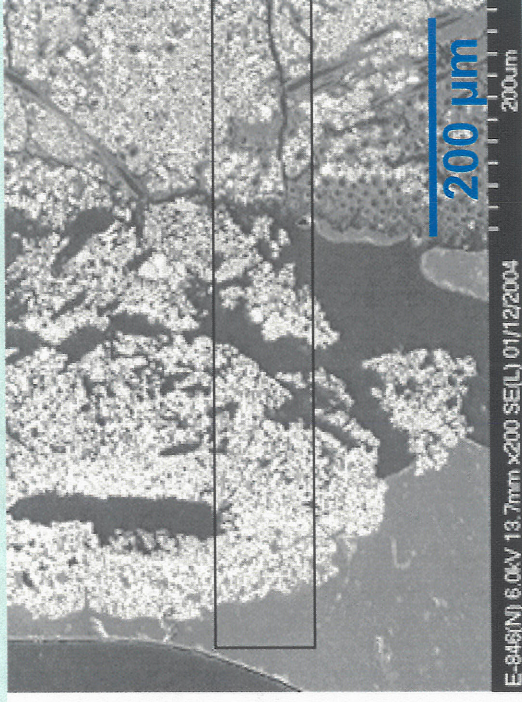
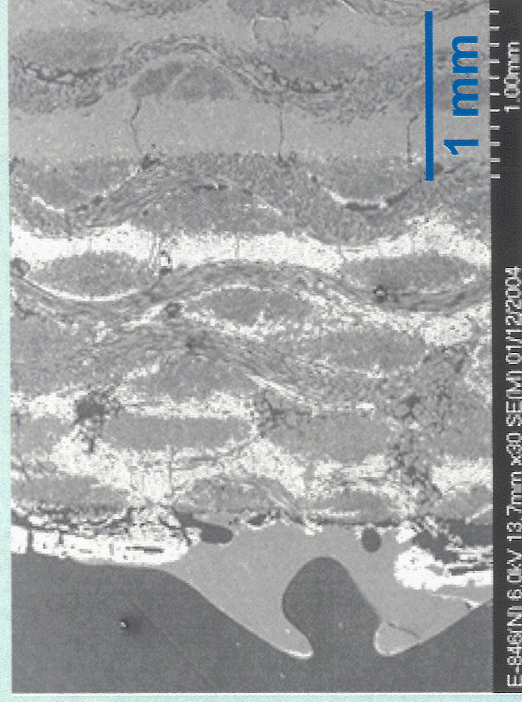
One 4-Minute Cycle to 1805°C



Three 4-Minute Torch Cycles to 1815 to 2015°C

- ◆ Coating consumption
- ◆ Carbon fiber oxidation

UHTC Side, Center Hot Zone Cross-Section



Conclusions

◆ Processing

- Uniform microstructure achieved with the C/SiC side having a Si-O-C plus SiC matrix and the UHTC side having a Si-O-C plus HfB₂ matrix.
- Matrix cracking due to thermal expansion mismatch between the carbon fibers and the matrix constituents is an area of concern.

◆ Mechanical Properties

- Flexural strength was close to expected values based on beam theory and the rule of mixtures with no matrix contribution.
- There was some evidence of composite behavior.

◆ Furnace Oxidation

- Carbon fiber oxidation occurred rapidly at cut edges and through cracks
- A seal coat is needed on the C/SiC side and a more oxidation resistant coating is required on the UHTC side of the composite.

◆ Torch Test

- Based on observed temperature spikes during test, adherence of the HfO₂-rich scale is an area of concern
- Material withstood ~2000°C (~3600°F), severe heat-up and thermal gradients with no major visible distress, but with significant HfB₂ coating and carbon fiber oxidation revealed by metallography

Recommendations

- ◆ Use fiber coatings to address fiber oxidation issues.
- ◆ Use advanced SiC fibers to address oxidation and thermal expansion mismatch issues.
 - Use temperature concerns with SiC fibers are mitigated by the thermo-mechanical loads on a typical leading edge. Compressive stresses are prevalent at the leading edge and tensile stresses are prevalent in the cooler regions.
- ◆ Improve oxidation resistance by limiting SiC content, raising the processing temperature to produce purer SiC from the polymeric precursor, and providing HfB_2 or another boron source throughout the composite.
- ◆ Net shape fabrication to avoid machined edges.



Acknowledgements

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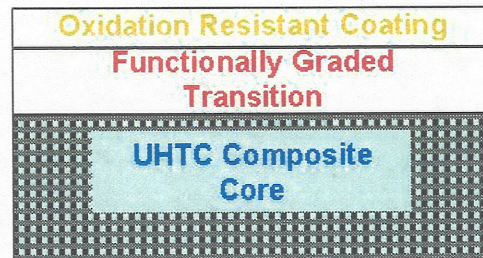


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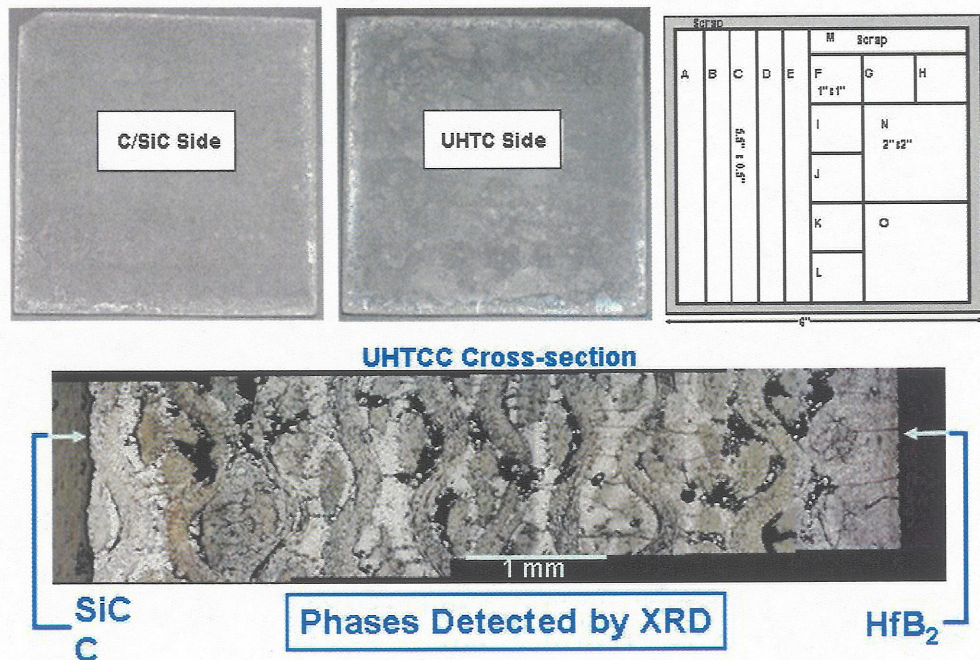
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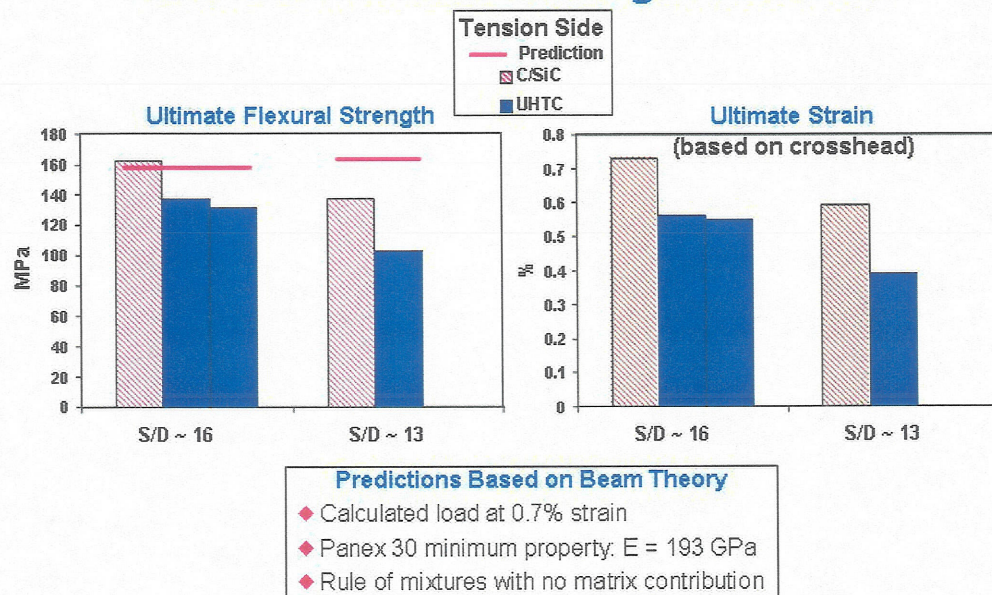
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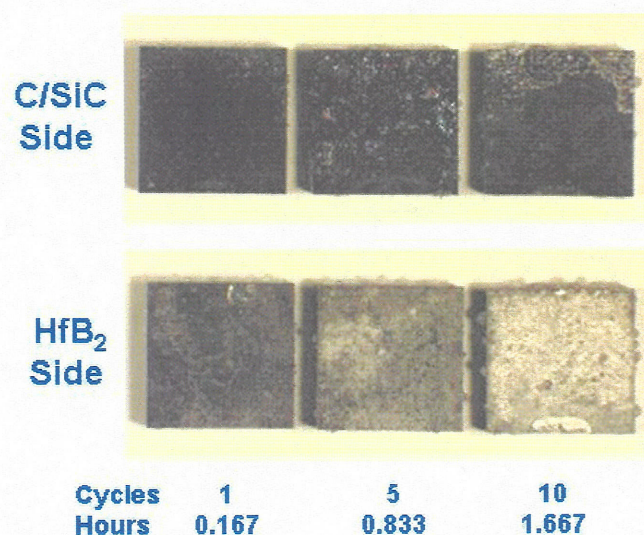
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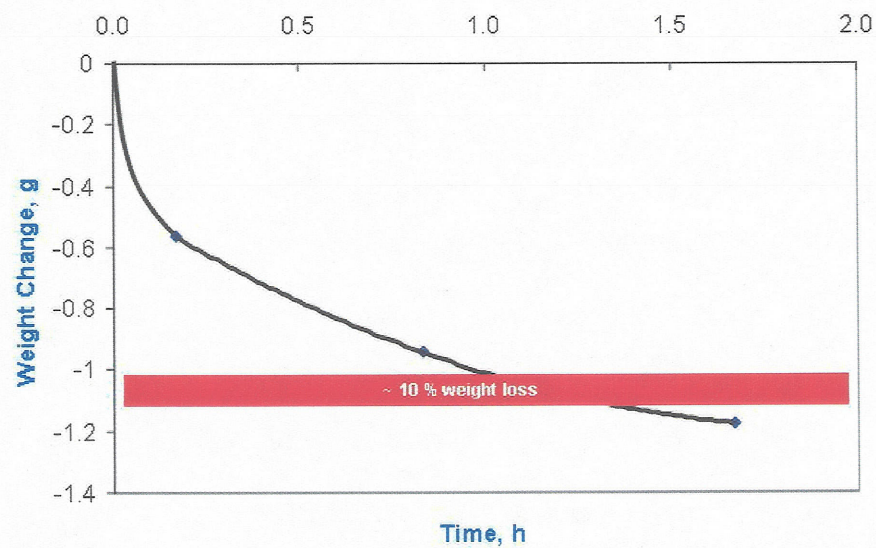
UHTCC Flexural Strength Results



UHTCC After 1627°C Furnace Oxidation

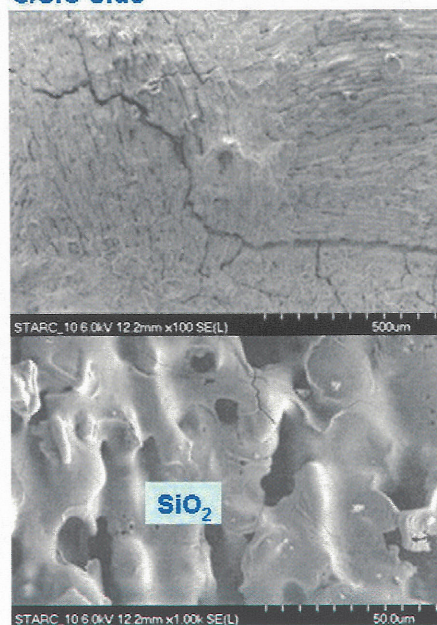


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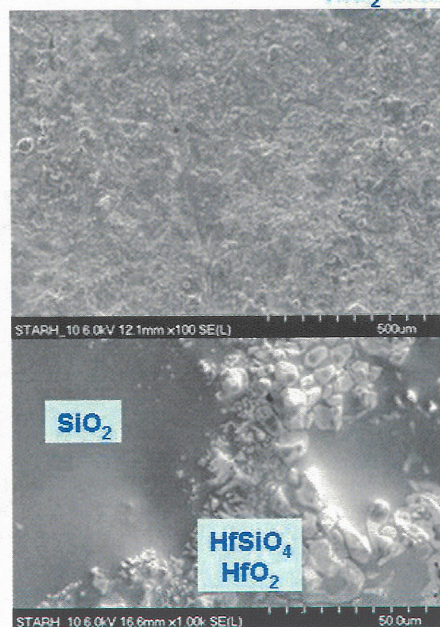


UHTCC After 10 Ten-minute Furnace Oxidation Cycles in Air at 1627°C

C/SiC Side



HfB₂ Side



UHTCC Oxy-Acetylene Torch Test

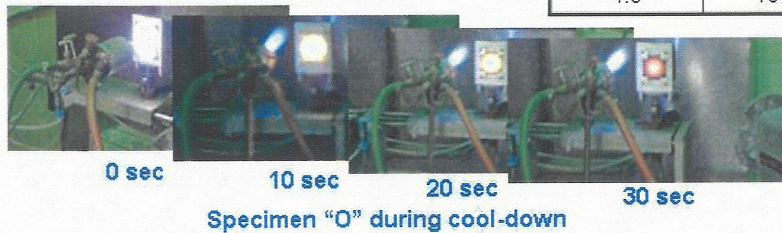
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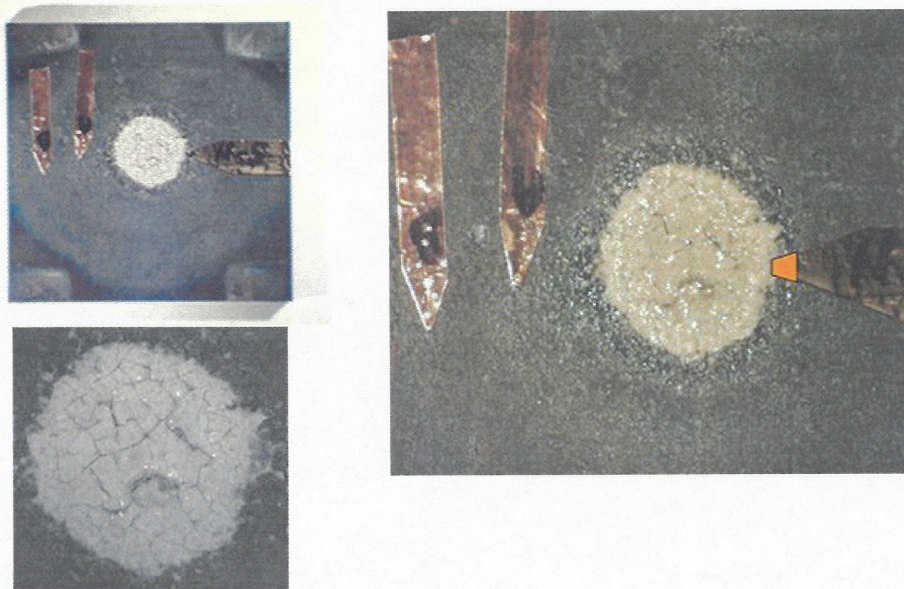
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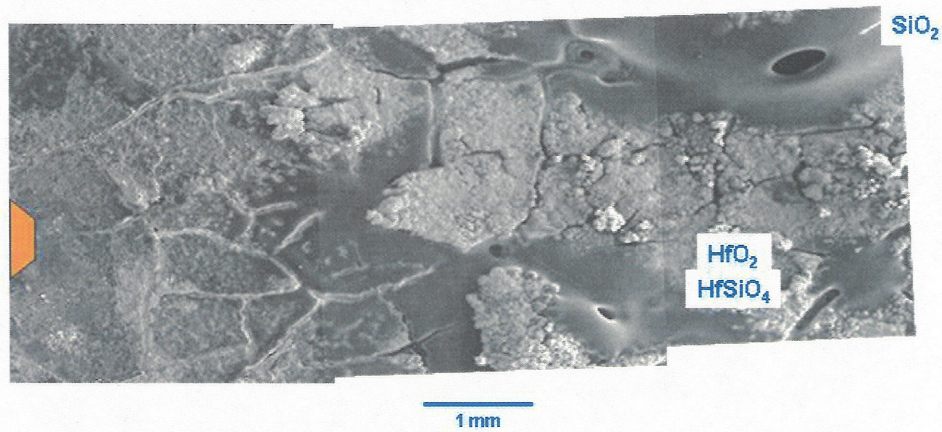
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UHTC Surface After Three 4-Minute Torch Cycles to 1815 to 2015°C

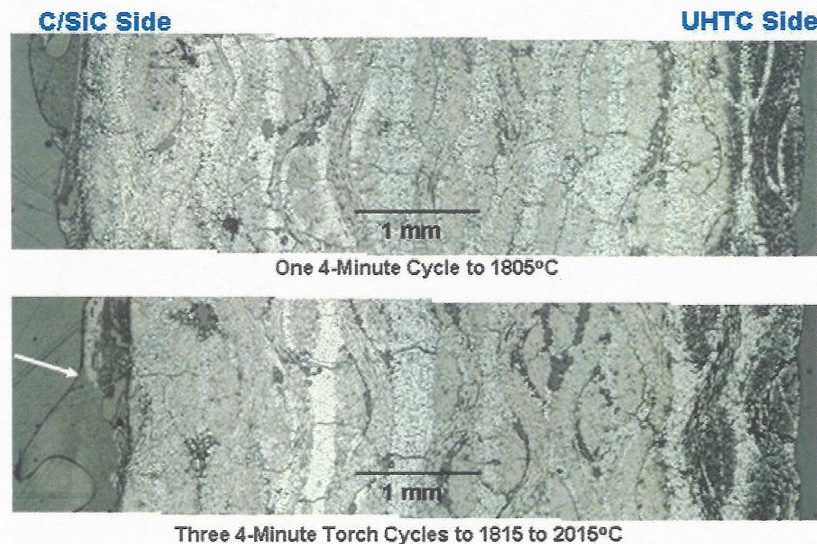


SEM of Center of UHTC Surface After Three Torch Cycles



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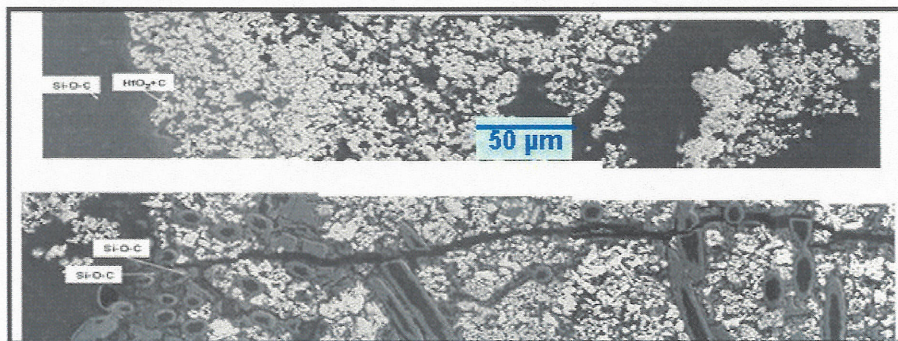
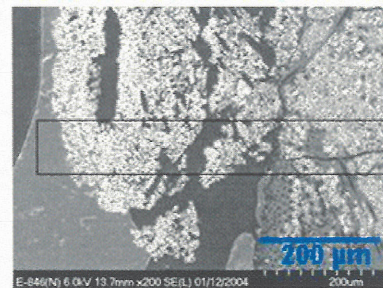
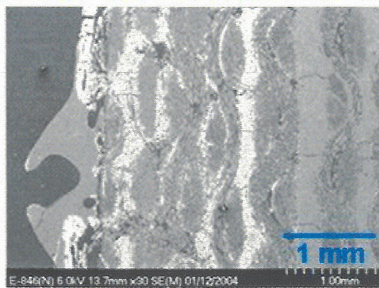
UHTCC Cross-sections After Torch Exposures



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